BMI-272

Subject Category: METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

THE IDENTIFICATION AND DISTRIBUTION OF INCLUSIONS IN DERBY AND INGOT URANIUM

By
C. M. Schwartz
D. A. Vaughan

August 31, 1953

Battelle Memorial Institute
Columbus, Ohio

Technical Information Service, Oak Ridge, Tennessee

Date Declassified: December 10, 1955.

Printed in USA, Price 20 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

X-18012

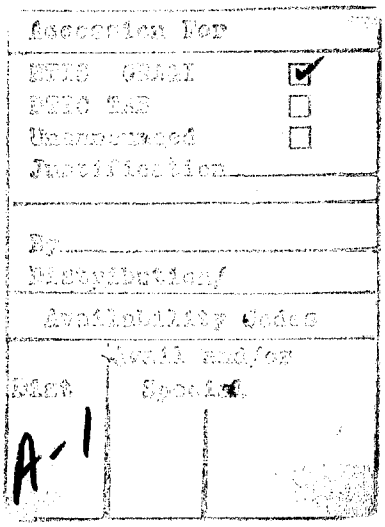
Report No. BMI-272

Contract No. AT-(30-1)-Gen-228

THE IDENTIFICATION AND DISTRIBUTION OF INCLUSIONS IN DERBY AND INGOT URANIUM

by

C. M. Schwartz
D. A. Vaughan



August 31, 1953

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

TABLE OF CONTENTS

ABSTRACT

Inclusions in derby and ingot uranium have been identified by X-ray diffraction methods. Metallographic and microradiographic examinations have shown that inclusions of MgF_2, UO_2, UN, and UO are concentrated at the top of derby and ingot metal by gravity separation. UC inclusions are distributed throughout the ingot metal. The amount of the carbide phase in the ingot varies with the temperature maintained during remelt of derby metal.

INTRODUCTION

This report describes the results of examination of specimens of derby and ingot uranium to identify inclusions and to study their distribution throughout the metal. The specimens were furnished by Mallinckrodt Chemical Works from production and pilot-plant runs of material prepared by bomb reduction of UF_4 by magnesium metal. Sufficient heat is liberated, in this highly exothermic reaction, to liquefy the reaction products, uranium metal plus MgF_2. The molten MgF_2 rises to the top as a slag, the uranium collecting in the bottom. Upon solidification, the slag (MgF_2 plus residual uranium compounds and impurities) is mechanically separated from the "derby". The derby is induction melted in graphite crucibles, in vacuum, and cast into graphite molds. Present production practice is to crop the top 5 in. from the 45-in. casting to remove the region of high porosity and high concentration of impurities.

In view of the relatively short time during which the bomb reaction products are liquid, and because of lack of stirring, it would not be surprising that the separation of metal and slag is incomplete, particularly in the top portion of the derby. Lack of separation was readily apparent by low-power microscopical examination of sections from the tops of derbies, simply prepared by surfacing with abrasive paper. The larger inclusions appeared to consist of spherical or irregularly shaped slag aggregates containing metal droplets. There was also a concentration of inclusions in the tops of recast metal (ingot).

The present investigation was initiated by Mallinckrodt with the objective of identifying the inclusions by X-ray diffraction. It later proved desirable to study the distribution microscopically and by microradiography, for correlation with the X-ray data. It was hoped that this information would aid in modifying production methods so that metal soundness would be increased while maintaining yield.

EXPERIMENTAL PROCEDURE

Several specimens taken 5 in. below the top of 45-in. ingots of uranium were abraded on 600-grit paper to show large (20 to 200 microns) inclusions and were submitted to Battelle by Mallinckrodt Chemical Works for X-ray diffraction identification of the inclusions. Examination under a

54X binocular microscope allowed sufficient working distance to extract the inclusions, with a needle probe, for powder X-ray diffraction analysis. Several of each type of inclusion were mechanically extracted and identified.

The large number of inclusions observed on the surface after coarse abrasion suggested that a further study be made of their distribution in bulk by microradiographic methods. Furthermore, the appearance of the surface in the low-power microscope indicated the need for metallographic examination for detection of finer inclusions.

Microradiographs were made of thin sections, 0.003 to 0.006 in. thick, at 45 kvp and 10 ma; a tungsten-target X-ray tube was used. Type-V spectrographic plate was placed in contact with the specimen at a 10-in. distance from the focal spot of the X-ray tube. The negatives were photographically enlarged 10 diameters.

The metallographic specimens were prepared as follows: Flat surfaces were prepared by dry grinding through 600-grit silicon carbide papers. The specimens were next polished on a high-speed wheel covered with Forstmann's cloth, using Linde B abrasive suspended in a 1 volume per cent chromic acid solution in water. They were next electropolished in a solution of 1 part stock (100 g CrO_3 in 100 cm^3 water) plus 4 parts glacial acetic acid; the stirred electrolyte was maintained cold in a bath of solid CO_2 in 1 : 1 ethyl alcohol - water. A potential of 60 v, rectified ac, was applied for 3-sec periods and repeated about 3 times, with intermediate rinsing in warm water and drying. The specimens were examined without etching; the above procedure appears to leave the surface slightly etched.

Metallographic and microradiograhic methods revealed many inclusions smaller than had been previously extracted mechanically. In order to identify these small inclusions, most of which were under 20 microns in diameter, surface-reflection X-ray methods were employed. The small inclusions were relief polished to increase the apparent concentration of this phase seen by the X-ray beam at grazing angles. The relief effect was produced by mechanical polishing followed by electropolishing for a short time in a chromic acid - acetic acid bath.

RESULTS

The uranium used in this investigation was supplied by Mallinckrodt Chemical Works from current production. In general, the samples were of three types: (1) derby metal, (2) cropped tops from vacuum-cast ingots,

and (3) top and bottom from the usable portion of the ingot. Table 1 describes the several samples submitted for study of the distribution and identification of inclusions.

MgF_2 and UO_2 comprise the majority of the 20- to 200-micron inclusions in the tops of both derby and ingot metal. Table 2 describes the visual appearance of these pin-point inclusions and gives the results of X-ray analysis of individual inclusions. The MgF_2 is concentrated in roughly spherically shaped cavities and has the characteristic crystalline appearance of the salt. The MgF_2 found in derby metal is sometimes white but frequently discolored (amber, red, or dark brown), depending upon the amount of UO_2 mixed with it. However, the MgF_2 found in the top of the ingot is usually grayish white or light amber and contains much less UO_2 than do the MgF_2 inclusions of derby metal. UO_2 is also found in rod- or curved-shaped cavities that usually contain some UO.

Figures 1 and 2 show the distribution of inclusions in tops of derby and ingot uranium. Large MgF_2 inclusions, together with many small inclusions, are apparent in both materials. However, the small inclusions are distributed differently. Table 3 gives the results of surface-reflection X-ray diffraction examination of the phases seen in relief in the microstructures. The microinclusions uniformly distributed in Figure 1 have been identified as UN. The clusters in the top of ingot metal, Figure 2, have been identified tentatively as UO, for reasons given in the next section. This phase is frequently associated with the MgF_2 inclusions in the top of ingot metal but not in derby metal.

The inclusions in derby metal, Figure 1, are concentrated in the top 1/2 in. but decrease in number below this top layer, as shown in Figures 3 and 4. The inclusions below the top layer are too few in number to be identified by X-ray diffraction. In the case of ingot metal, however, the inclusions are not as completely segregated as in the case of derby metal. Figure 5, a micrograph of a section just below the 5-in. cropped layer, shows a significant number of MgF_2, UO, and UC inclusions. The UC is undoubtedly formed by carbon pickup from the crucible during remelt and was detected by X-ray methods only in ingot metal. MgF_2 is absent in the bottom of the ingot and UO is greatly decreased, as shown in Figure 6. The angular phase seen as discrete particles in this micrograph has been identified by X-ray diffraction as UC.

Two samples of ingot metal prepared from pickled derbies were submitted to determine the effect of the pickling treatment on the number of inclusions retained in the ingot. In addition, the effect of holding temperature during remelt was studied with respect to amount of carbide formation in the ingot. Figures 7 and 8, micrographs of sections of ingots from pickled derbies remelted at 2450 F and 2800 F, respectively, show a

TABLE 1. DESCRIPTION OF SAMPLES OF URANIUM USED IN THE STUDY OF INCLUSIONS

Sample		Type of Uranium and Location of Sample with Respect to the Casting
BMI	MCW	
156A	9971-1	Vacuum-cast ingot - sampled 5 in. from top (cropped metal)
162A	9971-2	Ditto
158A	7 - 5	"
165A	12-1	"
157A	16-5	"
160A	40-3	"
163A	643T1	"
174A	1018[a]	"
175A	1469[a]	"
193A	1820T	Vacuum-cast ingot - sampled just below 5 in. cropped metal
194A	1820B	Vacuum-cast ingot - sampled at the bottom of ingot
171A	1020	Derby metal - extreme top of pilot-plant derby
172A	742T	Derby metal - 2 in. from top of regular production derby
173A	742B	Derby metal - 2 in. from bottom of regular production derby

(a) The derby metal used for these two ingots was pickled before remelting. Ingot 1018 was remelted at 2450 F and Ingot 1469 was remelted at 2800 F; both were cast at 2525 F.

TABLE 2. DESCRIPTION AND IDENTIFICATION OF PIN POINT[a] INCLUSIONS IN TOPS OF DERBY AND INGOT URANIUM

Casting	Inclusion (X-Ray) No.	Description of Material in Inclusion	Phases Identified[b]
9971-1	156B	White crystalline salt	S-MgF_2 + F-CaF_2 + F-UO
	156C	Gray powder from sides of voids	S-UO_2 + F-U + F-MgF_2
	156D	Brown, glassy salt from shallow rod-like inclusion	S-UO_2 + M-UO
	156E	White and black salt from various inclusions	S-UO_2 + MS-MgF_2
	156F	Similar to 156B	S-MgF_2 + MF-MgO
9971-2	162B	Scraping from gold-colored sides of void	S-U + M-UO_2
	162C	Loose shell of metal within void	S-U
	162D	Similar to 162B	U + UO_2 + UO
7-5	158A	Gray crystalline salt	S-MgF_2 + F-UO_2 + F-UO
	158B	Reddish-brown salt	M-MgF_2 + M-UO_2 + M-UO
	158C	Gray-metallic material	S-"X"[d]
12-1	165A	Dark, gray, granular material in curved-shaped inclusion	S-UO_2 + M-UO
16-5	157A	Dark, soft, granular material	S-UO_2 + M-UO
	157C	Ring having metallic luster when polished; brown when scraped	S-UO_2 + MS-UO
1020[c]	171B	Loose powder in void (black)	U + diffuse UO_2 + SiC
	171C	White salt	S-MgF_2 + VF-UO_2
	171D	Amber salt	S-MgF_2 + F-UO_2
	171E	Dark, amber salt	S-MgF_2 + MF-UO_2
	171F	Reddish-white salt	S-MgF_2 + MF-UO_2
	171G	Brown salt mixed with white	S-MgF_2 + M-UO_2
	171H	Black	S-MgF_2 + F-"X"
	171I	Bright metallic (ductile)	S-Mg

(a) Pin-point inclusions are those larger than 20 microns in diameter.

(b) The following abbreviations are used to indicate relative intensities of the various phases and not to represent estimates of amounts of the phase present: S - strong, M - medium, F - faint, V - very.

(c) This sample was taken from the extreme top of pilot-plant derby.

(d) "X" is an unidentified phase, FCC with a_o = 5.68A.

TABLE 3. IDENTIFICATION OF MICROINCLUSIONS[a] IN DERBY AND INGOT URANIUM

Casting[b]	Sample No. (X-Ray)	Figure	Inclusion Phases Identified
9971-1	156	2	UO[c]
1018	174	7	UC
1469	175	8	UC
1820T	193	5	UC + UO[c]
1820B	194	6	UC
1020[d]	171J	1	UN

(a) These inclusions are less than 20 microns in diameter and are too small to extract by hand but can be relief polished electrolytically.
(b) The specimens were taken 5 in. from the top of the cast ingot except for 1820T and 1820B, which are from the top and bottom of ingot after 5 in. is cropped from the top.
(c) Lattice constant = 4.92A. This phase not distinguishable from U(C,N) by X-rays.
(d) Derby metal.

considerable decrease in the number of large inclusions (MgF_2) compared with normal production ingot (Figure 2). UC was the only phase detected by X-ray diffraction examination of these two samples; the ingot held in contact with the carbon crucible at the higher temperature gave a much stronger pattern of UC. The significant increase in size and number of angular carbide particles is apparent in the micrographs. The clusters of dark etching particles are probably not UC. These, while not identified by X-ray diffraction, have the characteristic appearance of the UO phase identified in Figures 2 and 5. The X-ray studies were made on these samples after an extra long (30 sec) electropolish, which removed the clusters identified as UO in other samples.

Very fine inclusions, which appear to outline grains, are also shown in the photomicrographs, Figures 2 through 8. The phase comprising these inclusions has not been identified. There is evidence that the apparent number of these inclusions varies with polishing and etching techniques, although this observation has not been confirmed.

Interpretation of the microradiographs of Figures 2 through 8 is difficult, owing to artifacts caused by sample preparation. Mottling caused by uneven polishing (Figures 5a, 6a, and 7a) and scratches are very difficult to eliminate in these thin sections. Furthermore, the large difference in X-ray absorption between the slag and metal requires overexposure of the large slag inclusions in order to penetrate the more absorbing metal. The overexposure causes excessive fogging adjacent to the inclusion, as shown in Figure 8.

DISCUSSION OF RESULTS

A considerable number of the inclusions found in the top 5 in. of ingot uranium consists of slag "carry over" from the derby metal. In a previous investigation* of the constitution of bomb slag, it was found that the MgF_2 slag adjacent to the derby contained a high percentage of UO_2. Based on this observation and on the absence of nitrides in the slag, it was then concluded that the UO_2 formed mainly by reaction of metal with constituents of the refractory liner rather than with the atmosphere. However, in the present study, nitride was found in the top of the derby. The only likely source of nitrogen is air, either trapped in the charge or, more probably, considering the location of the nitride in the metal, sucked in during cooling of the bomb.

In normal production of ingot metal, the impurities trapped in the derby are carried over into the remelt. An additional impurity, carbon, is picked up from the graphite crucible during remelting. Of these impurities, MgF_2 and UO_2 are found concentrated in the top 5 in. of the ingot; the carbon forms UC and is distributed throughout the ingot. UN, identified in the top of derby metal, has not been found in the ingot but may be present as carbonitride, not identifiable in the presence of UO, as discussed later. The phase identified as UO is concentrated in the cropped top of the ingot. From the above remarks, it should not be inferred that the impurity concentration decreases sharply 5 in. below the top. As noted in Table 1, only two samples below the cropped portion were supplied, and the distribution below this level was not studied. However, microscopical examination of longitudinal sections of ingots by Mallinckrodt** showed that slag inclusions are found throughout the upper third of the ingot.

---

*Vaughan, D. A., Cocks, G. G., and Schwartz, C. M., "Identification of Slag Constituents from Uranium Metal Production Bombs", BMI-258.

**Ruehle, A. E., et al., Research and Development Progress Reports NYO 1352 and NYO 1354.

Identification of the phases indicated in Tables 2 and 3 is unequivocal on the basis of the X-ray diffraction patterns alone, with the possible exception of UO. This is the intermediate member of the series of isomorphous compounds, UN, UO, and UC, face-centered cubic, with lattice constants a_o, of 4.890A, 4.920A, and 4.961A, respectively.* These compounds are reported to be mutually soluble in all proportions. Obviously, the carbonitride, U(N,C), containing approximately equimolar quantities of carbon and nitrogen has a lattice constant about equal to that of UO and is not distinguishable from the latter by X-ray diffraction methods. Identification of UN and UC is considered unequivocal on the basis of their measured lattice constants.

In the case of the specimens of Table 2, which were individually picked out of inclusions, the location of the actual X-ray specimen with respect to the phases associated with it is known. Here, the phase yielding the 4.92A lattice constant is in contact with UO_2 and metal, and it is reasonable to conclude that the phase is mainly UO, by reduction of UO_2. Further evidence of localized partial reduction of UO_2 inclusions during remelting is obtained from microscopical inspection, Figure 2. This shows the tendency of the UO phase to form in clusters adjacent to MgF_2 inclusions. Furthermore, the MgF_2 inclusions, most of which are discolored in derby metal, are in general considerably whitened after remelting, suggesting loss of UO_2 while in contact with the molten metal.

The identification of the microinclusions UN, UO, and UC is based upon X-ray spectrometer data from specimens metallographically prepared to leave the microinclusions in relief. In Table 3, the pattern with lattice constant 4.92A, obtained from ingot, is interpreted as that of the phase UO. The pattern is certainly due, in part, to the clusters around MgF_2 inclusions (e.g., in Figure 2); the clusters, therefore, are probably mainly UO. However, to account for the nitrogen in the derby and the carbon introduced during remelt, the possible presence of some U(C,N) must not be ignored.

CONCLUSIONS

1. The inclusions concentrated near the top of ingot metal are a carry-over of slag on the surface and in the first 1/4-in. layer of derby.

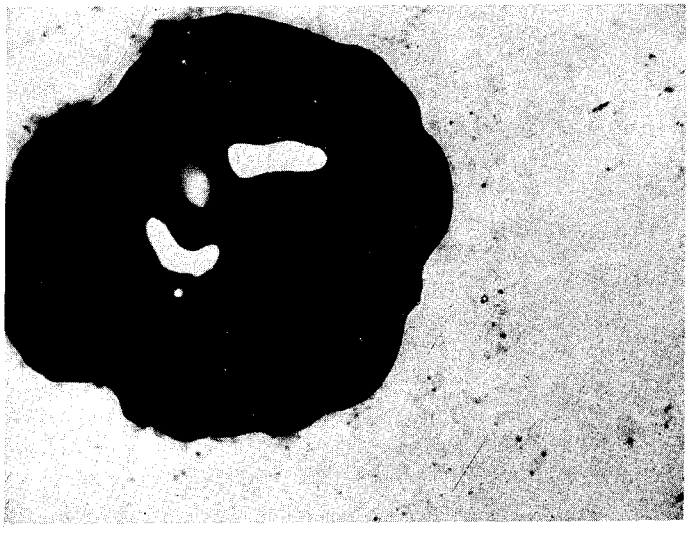
2. The amount of slag carry-over is appreciably reduced by nitric acid pickle of the derby before remelting.

*Rundle, R. E., Baenziger, N. C., Wilson, A. S., and McDonald, R. A., "The Structures of Carbides, Nitrides, and Oxides of Uranium", J. Am. Chem. Soc., 70, 99 (1948); Rundle et al., "Summary of X-Ray Information on Hydrides, Deuterides, Carbides, Nitrides and Oxides of Uranium", CC2397, February, 1945.

3. The major inclusion in the usable portion of ingot metal is UC, a pickup during remelting in the carbon crucible. The amount of carbide inclusion in ingot metal varies with temperature of remelting.

The authors wish to express their appreciation to A. F. Gerds for his preparation of the photomicrographs, to J. R. Doig for preparation of the microradiographs, and to G. G. Cocks and M. W. Mallett for their valuable suggestions.

300X N3994



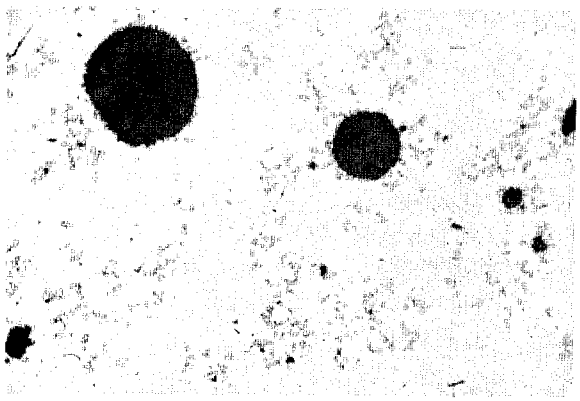
500X N3995

FIGURE 1. PHOTOMICROGRAPHS OF A SECTION OF TOP OF DERBY METAL (1020)

Large MgF_2 inclusions and uniformly distributed microinclusions of UN are seen.

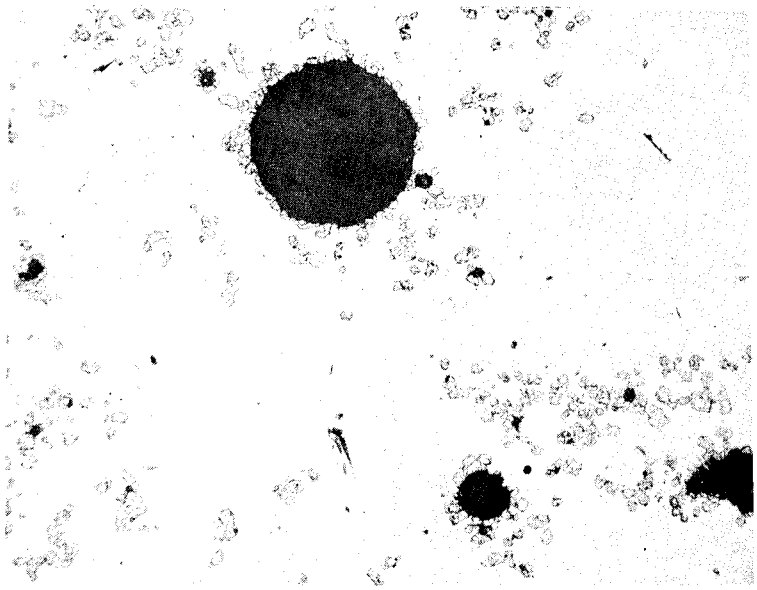
10X 168A22

a. Microradiograph



100X N4016

b. Photomicrograph



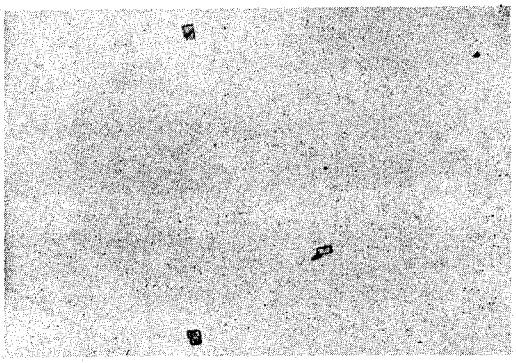
250X N4014

c. Photomicrograph

FIGURE 2. SECTION OF 5-IN. CROPPED TOP OF INGOT 9971 SHOWING DISTRIBUTION OF LARGE MgF_2 INCLUSIONS AND CLUSTERING OF UO MICROINCLUSIONS AROUND THEM

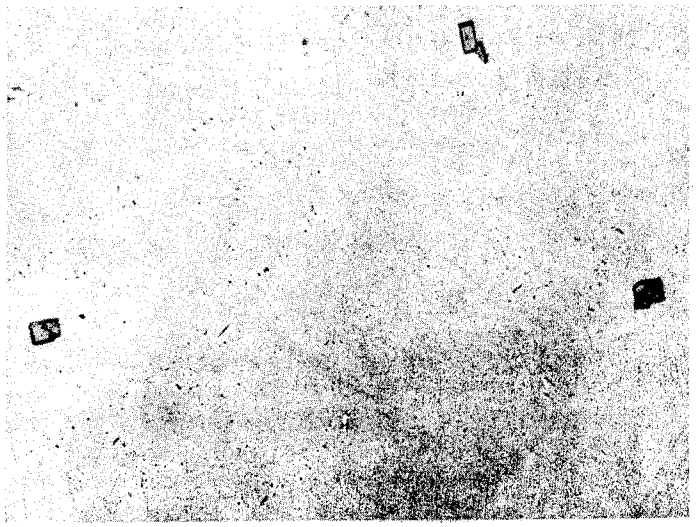
10X 178A1

a. Microradiograph



250X N4007

b. Photomicrograph

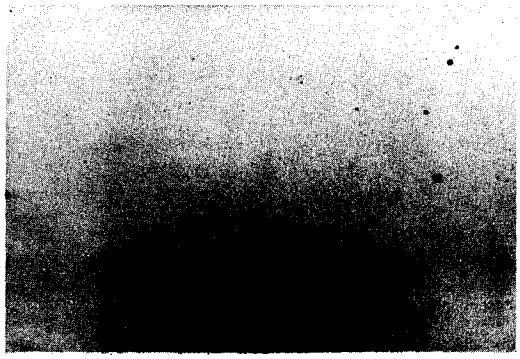


500X N4006

c. Photomicrograph

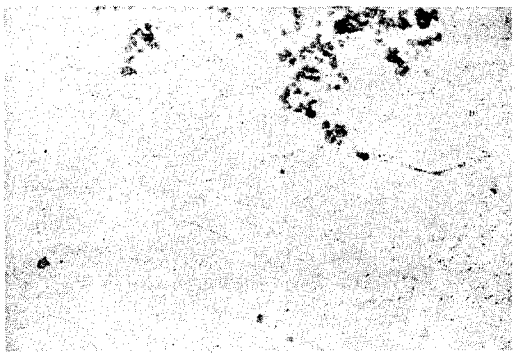
FIGURE 3. SECTION OF DERBY 742T 2 IN. FROM TOP SHOWING ABSENCE OF LARGE MgF_2 INCLUSIONS

A few angular microinclusions believed to be UC are present. The fine structure seen as pseudo grain-boundary inclusions is well shown in c; this phase has not been identified.



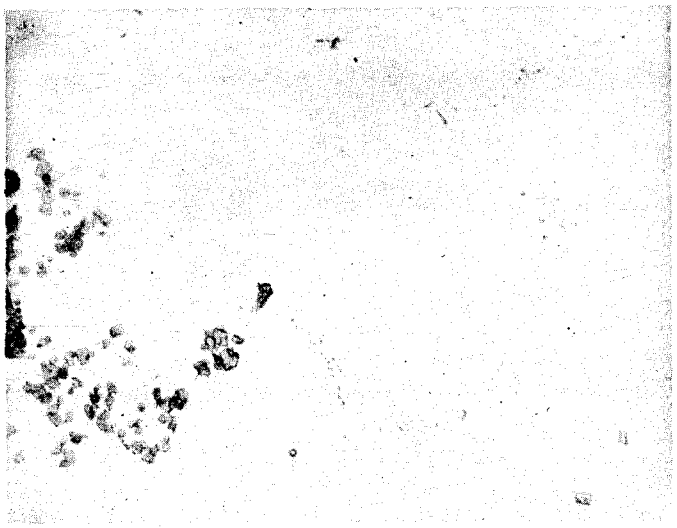
10X 179A4

a. Microradiograph



250X N4002

b. Photomicrograph

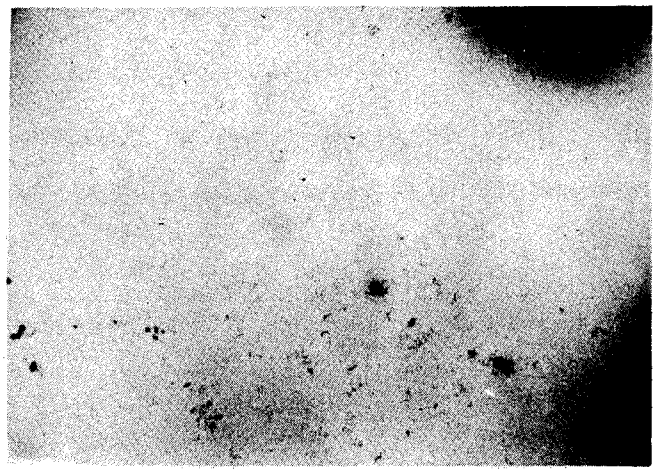


500X N4003

c. Photomicrograph

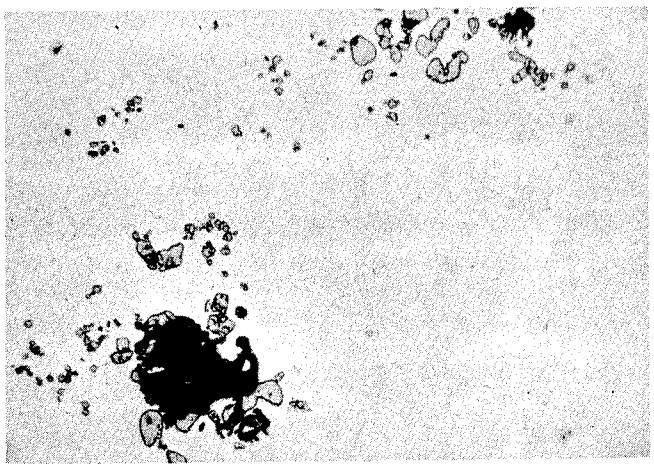
FIGURE 4. SECTION OF DERBY 742B 2 IN. FROM THE BOTTOM SHOWING ABSENCE OF LARGE MgF_2 INCLUSIONS

Small inclusions visible in microradiograph, a, are believed to be the resolved clusters of microinclusions in photomicrographs b and c. These have the characteristic appearance of the phase identified as UO.



10X 193A2

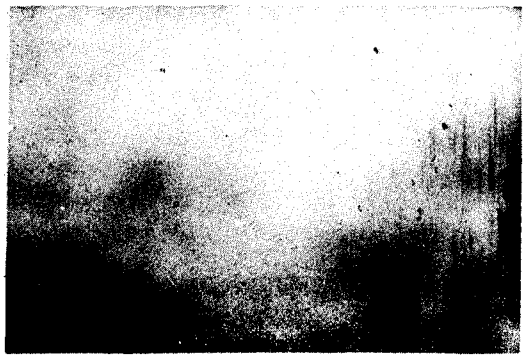
a. Microradiograph



250X N4000

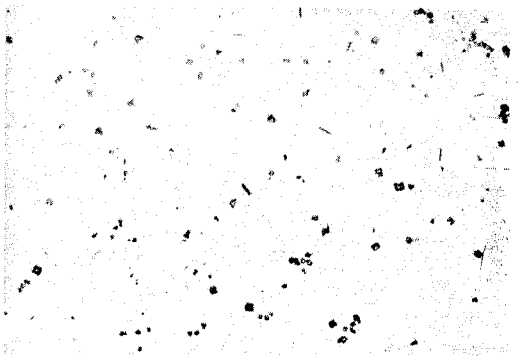
b. Photomicrograph

FIGURE 5. SECTION OF INGOT 1820T JUST BELOW CROPPED PORTION SHOWING A NUMBER OF MgF_2 INCLUSIONS PLUS CLUSTERS OF UO AND DISCRETE PARTICLES OF UC



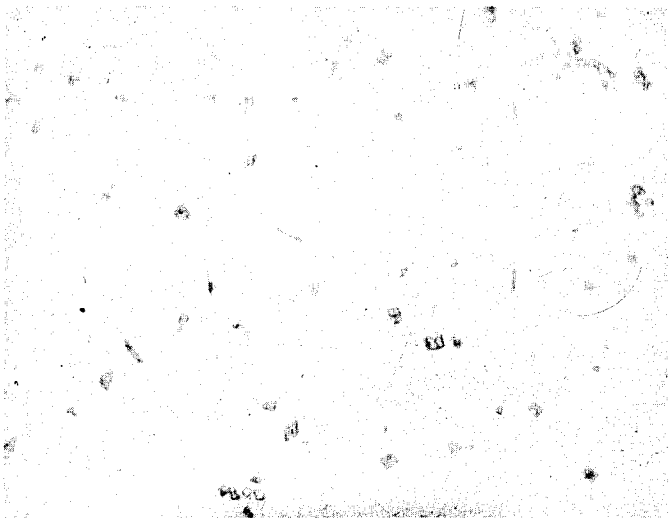
10X 194A2

a. Microradiograph



250X N4004

b. Photomicrograph



500X N4005

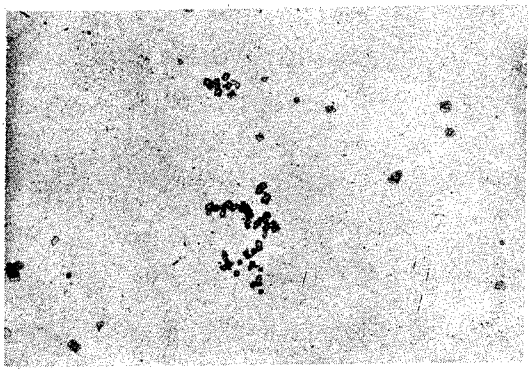
c. Photomicrograph

FIGURE 6. SECTION FROM BOTTOM OF INGOT 1820B SHOWING ABSENCE OF MgF_2 INCLUSIONS

The angular microinclusions have been identified as UC. A few clusters of the phase identified as UO are apparent in b and c.

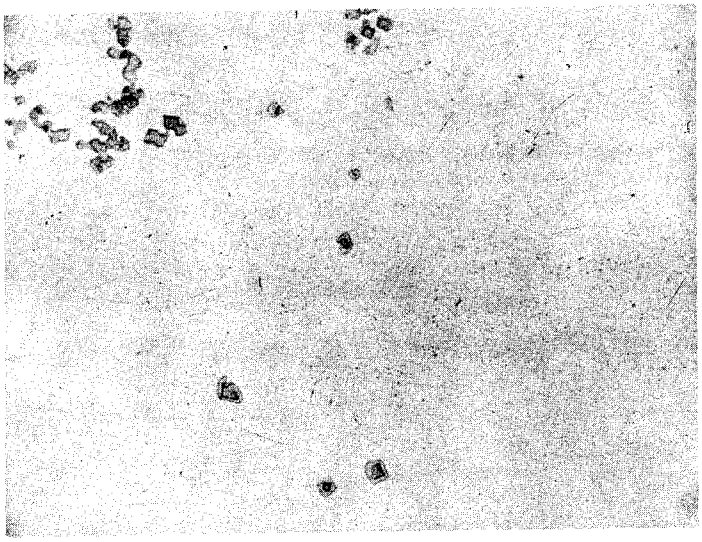
10X 174A2

a. Microradiograph



250X N4013

b. Photomicrograph



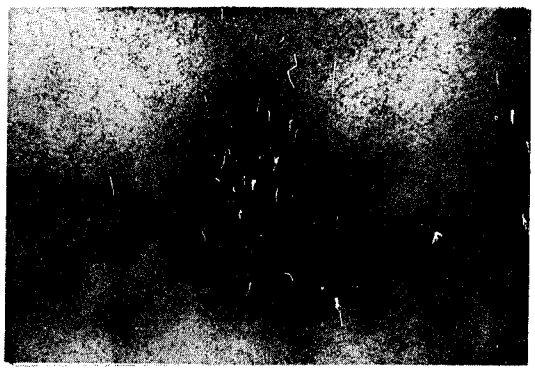
500X N4012

c. Photomicrograph

FIGURE 7. SECTION OF CROPPED INGOT 1018 MADE FROM PICKLED DERBIES

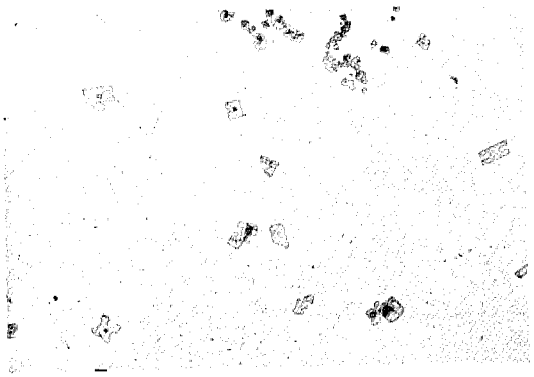
Only a few MgF_2 inclusions are seen in a. Clusters of UO and discrete angular particles of UC are shown in b and c.

GPO 822171 - 2



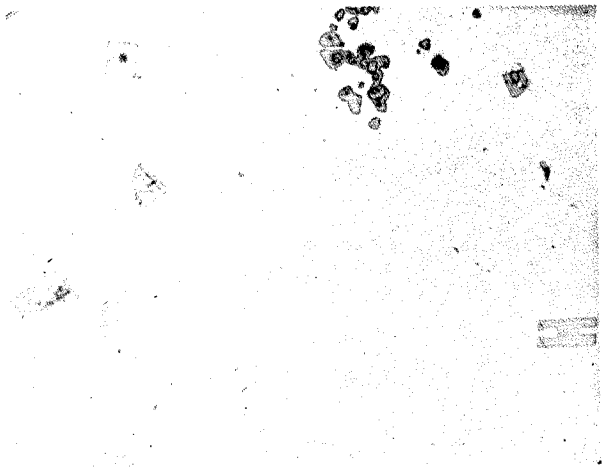
10X 175A2

a. Microradiograph



250X N4010

b. Photomicrograph



500X N4011

c. Photomicrograph

FIGURE 8. SECTION OF CROPPED INGOT 1469 MADE FROM PICKLED DERBIES

Only one MgF_2 inclusion is evident in a. The uniform fine structure seen in a is believed to be the large angular UC phase and/or clusters of UO shown in b and c.

GPO 822171 - 1